

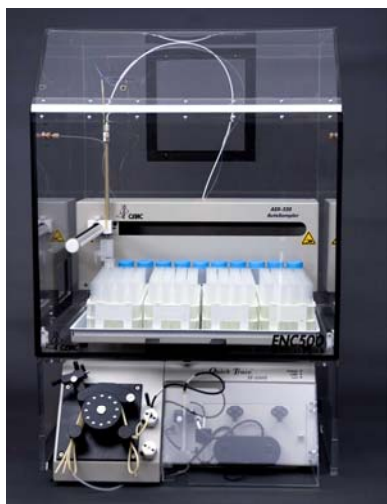
Mercury Determination in Water, SRM 1641c, EPA Method 245.7, using the CETAC QuickTrace™ M-8000 CVAFS

Jeff Forsberg, Product Manager, Maggie Day, Product Specialist, CETAC Technologies, Omaha, NE

INTRODUCTION

Total mercury determination in water allows quantitation for many different applications. The goal of this specific application is to validate the QuickTrace™ M-8000 Mercury Analyzer Fluorescence Spectrometer by analyzing SRM 1641c, Mercury in Water. The standard reference material was digested according to EPA Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, Rev. 2.0. Mercury contamination is prevalent as different species throughout various water sources. Measuring the amount of mercury contamination in these sources is important for preservation and overall health of the environment. Detection is dependent on instrument stability and sensitivity.

INSTRUMENTATION



The QuickTrace™ M-8000 Mercury Analyzer Fluorescence Spectrometer is a standalone mercury analysis system. The instrument working range is from < 0.05 ppt to > 400 ppb, and is dependent on instrument settings. The large working range of the system allows for analysis at the ultra-trace level up to very high concentrations.

The QuickTrace™ M-8000 is accompanied with an autosampler that allows for hands-free sample batch analysis. The four-channeled, 12-roller peristaltic pump ensures consistent sample/reagent uptake in a closed system. The sample is reduced by the online addition of stannous chloride. The reduced sample then flows into the patented gas-liquid separator (GLS) where the elemental mercury is libe-

rated from the liquid stream as vapor, flows through the Nafion® dryer where excess moisture is removed and then flows into the analyzer. The sample is excited by a mercury vapor lamp at wavelength 253.7nm and emission is detected by the photomultiplier fluorescence detector, and quantitated in the QuickTrace™ software. Software instrument controls include but are not limited to argon flow, lamp, detector voltage, pump control and smart rinse threshold. Instrument parameter optimization allows analysis with increased or decreased sensitivity.

EXPERIMENTAL

The standard reference material, SRM 1641c, Mercury in Water, is certified for 1.47 mg/L with an uncertainty of ± 0.04 mg/L, and was purchased from The National Institute of Science and Technology (NIST). The standard reference material was packaged in 10 mL ampoules. Proper dilution was prepared immediately prior to digestion to give a concentration within the working range of the QuickTrace™ M-8000. Dilution aliquots of the standard reference material were taken from a pre-cleaned polystyrene beaker to minimize contamination of the stock standard reference ampoule.

Conditions	
Gas Flow (ml/min)	Low Flow
Pump speed (%)	100
Sipper depth (mm):	145
Sample uptake time (s):	50
Rinse time (s):	95
Read delay time (s):	58
Replicate read time (s):	2
Replicates:	4
<input checked="" type="checkbox"/> Auto adjust replicate read time	
Profile Replicate %RSD:	0%

Figure 2. Method Parameters

Dilutions were made in pre-cleaned 50 mL polypropylene tubes. The tubes were soaked overnight in 10% trace-metal grade nitric acid and rinsed three times with mercury-free deionised water, rated at 18.2 M Ω . Samples were oxidized with 0.1N potassium bromide/potassium bromate solution. The bromine was reduced with 12% hydroxylamine hydrochloride. Inorganic mercury was reduced to elemental mercury by online addition of 10% stannous chloride in 7% hydrochloric acid. Seven replicates of the standard reference material were analyzed along with the appropriate quality control checks to validate the instrument. A seven point calibration was analyzed, and included five non-zero standards and two blanks.

CALIBRATION STANDARDIZATION

Calibration standards were prepared with appropriate aliquots of a 200 ng/L working mercury standard. This standard was prepared from correct serial dilutions of a 1000 mg/L certified mercury standard. Aliquots of 1.0 mL, 2 mL, 5 mL, 10 mL, and 20 mL of 200 ng/L were added to tubes containing ~ 10 mL of 3% HCl and brought to a final volume of 40 mL with 3% HCl for concentrations of 5, 10, 25, 50 and 100 ng/L respectively. Calibration standards were prepared in pre-cleaned 50 mL polypropylene tubes that were soaked overnight with 10% trace metal grade nitric acid. The tubes were then rinsed three times with ultra-pure mercury-free deionized water, rated at 18.2 M Ω . Each standard was matrix-matched with 0.5 mL of 0.1N potassium bromide/potassium bromate and 0.05 mL of 12% hydroxylamine solution. Two calibration blanks and five non-zero standards were analyzed starting with the lowest concentration standard. Peak height was integrated for a total of 8 seconds and %RSD and the calibration factor was calculated.

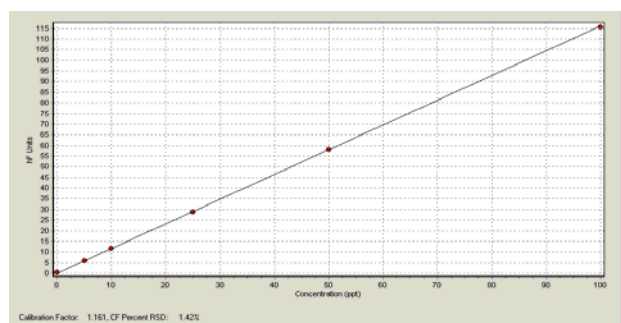


Figure 3. Method 245.7 Calibration

PROCEDURE

Dilutions were prepared from the standard reference material 1641c, Mercury in Water, to give a good working concentration for low-level analysis. An excess volume of the standard reference material was directly poured into a pre-cleaned 50 mL polystyrene beaker to minimize contamination. Dilutions were made with 0.1 mL aliquots of the standard reference material, and added to 40 mL of 3% hydrochloric acid to give a dilution factor of 400 and a concentration of 3.7 μ g/L. Serial dilutions were then made from the first dilutions by adding a 0.1 mL aliquot to pre-cleaned tubes containing 40 mL of 3% hydrochloric acid to give an expected concentration of ~ 9.6 ng/L. The final dilution factor for the digest solution was 160,000. The standard reference material was digested by oxidation with 0.5 mL of 0.1N potassium bromide/potassium bromate solution. The sample was allowed to sit for 30 minutes to ensure complete oxidation. The bromine was then reduced with 0.05 mL of 12% hydroxylamine hydrochloride. Inorganic mercury was reduced to elemental mercury by the excess online addition of 10% stannous chloride in 7% hydrochloric acid, at a volume of 3.8 mL/min. Peak height for each standard was integrated for a total of 8 seconds. The %RSD was calculated based on standard deviation and mean concentration for each sample. Initial calibration verification, initial calibration blank, quality control spike, matrix spike, and matrix spike duplicate were analyzed to validate the instrument. Initial calibration verification was prepared by adding a 0.1 mL aliquot of a 10 μ g/L secondary mercury standard to ~ 10 mL of 3% HCl and brought to a final volume of 40 mL with 3% HCl. The ICV standard was matrix-matched with 0.5 mL of 0.1N potassium bromide/potassium bromate and 0.05 mL of 12% hydroxylamine solution. The concentration was 25 ng/L. Quality control spike, matrix spike, and matrix spike duplicate were prepared in the same manor by adding 0.080 mL of a 10 μ g/L mercury working standard and matrix-matched with the addition of 0.5 mL of 0.1N potassium bromide/potassium bromate solution and 0.05 mL of 12% hydroxylamine. This gave a concentration of 20 ng/L.

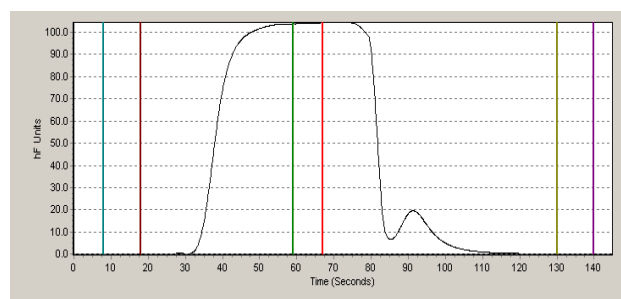


Figure 4. High Standard Peak Profile

RESULTS

Total mercury in SRM 1641c, Mercury in Water, was easily recovered and quantitated using the Quick-Trace™ M-8000 Mercury Analyzer Fluorescence Spectrometer. The results of 1.49 mg/L \pm 0.034 are shown in figures 5 and 6. An MDL of 0.15 ng/L was achieved following 40 CFR Ch.1 (7-1-91) Part. 136, App B using the procedure described in this application note. Pump speed, sample uptake, and argon flow were optimized for low-level analysis. Calibration, quality controls, and spike recovery were all analyzed to validate the Quick-Trace™ M-8000. SRM 1641c, Mercury in Water, is certified at 1.47 mg/L with an uncertainty of \pm 0.04 mg/L, and is based on a 95% confidence level. Even though the final dilution factor was 160,000 the results correlated extremely well to the certified value. The close correlation validates all aspects of the laboratory procedures and demonstrates clean room techniques in a non-clean room setting.

NIST Mercury In Water 1641c, 1.47 mg/L \pm 0.04	
Digest	mg/L
1	1.53
2	1.48
3	1.48
4	1.49
5	1.50
6	1.49
7	1.49
Mean = 1.49	
Uncertainty = 0.034	
n = 7 Replicates STD = 0.0172 RSD% = 1.150	

Figure 5. Dilution Corrected Results

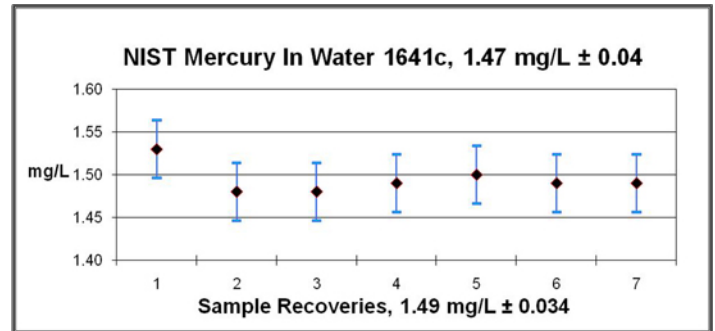


Figure 6. Dilution Corrected Results with Uncertainties

REFERENCES

EPA Method 245.7, Mercury in Water by Cold Vapor Atomic Fluorescence Spectrometry, Rev. 2.0.